Analysis of Coals from the San Juan Basin by Programmed Temperature Micropyrolysis

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Abstract

Eighteen coals from the San Juan Basin of the southwestern U.S. were analyzed by micropyrolysis at constant heating rates for temperatures of maximum evolution (T_{max}) and pyrolysis yields. T_{max} values increased with maturity (as measured by vitrinite reflectance [$\%R_m$]). The pyrolysis yields increased with increasing maturity until approximately R_m of 0.9% after which the yield declined rapidly.

A subgroup of coals from the Fruitland seam of the San Juan basin was also analyzed by micropyrolysis at several constant heating rates to determine laboratory pyrolysis kinetics. The kinetic calculations yielded the energy of activation by the approximate method (E_{approx}) and the principal energy of activation by the discrete method (principal $E_{discrete}$) in the range of 55 to 57 kcal/mol for the coals in the R_m range of 0.4 to 0.9%. However, the coal with the highest R_m (1.30%) had E_{approx} and principal $E_{discrete}$ around 63 kcal/mol.

These Fruitland seam coals were also extracted with organic solvents and the residual coals were analyzed to determine laboratory pyrolysis kinetics. The results were within experimental error of the kinetic values calculated for the corresponding unextracted coals.

Key words: San Juan Coals, Pyrolysis Kinetics, and Yield

Introduction

The San Juan Basin in the southwestern U. S. (Four Corners area) is a major producer of natural gas. Recently, there has been activity in the exploration for gas in the upper cretaceous Fruitland seam, which is the major deposit of coal in the basin. The Fruitland seam is considered to have the potential of 50-56 tcf of gas production, as well coal reserves of approximately 200 billion tons.[1]

Most of the production is probably due to the thermal maturation over geological time. To assist in the understanding of this hydrocarbon production, we have been studying thermal maturation of source materials in the laboratory by pyrolysis techniques,[2] such as the Pyromat II micropyrolyzer.[3] With this technique, the pyrolysis kinetics are measured, and through selected models, these kinetic parameters measured have been extrapolated to produce relevant maturation parameters.

This report summarizes pyrolysis kinetic analysis of selected coals from the San Juan Basin by the Pyromat II micropyrolyzer. A more complete listing and analyses of this data will be reported elsewhere.[4]

Experimental

Kinetic Analysis. The method of kinetic analysis using the Pyromat II has been described in detail elsewhere.[3] Briefly, the kinetics were determined from multiple runs at constant heating rates on approximately 4 to 10 mg samples. Generally three - 50°C/min, one - 7°C/min, and two - 1°C/min runs were performed. If T_{max} values and profile shapes were not in agreement, more runs at these heating rates were performed.

Yield Analysis. Yield analysis was performed on all samples by comparing to the yield of AP22 oil shale. This yield has been determined from Fisher Assay to be 88 mg of pyrolysate/gram oil shale. Two furnaces were used for these measurements. The yields were determined by two methods: 1) the yield was determined for the coal from two or three runs at the nominal heating rate of 25°C/min, from 250°C to 700°C using the old furnace. The AP22 standard was run twice daily and a single calibration factor was determined for the entire set of runs (over a period of four days). 2) For the four samples used in the kinetic analyses, several determinations were performed using the new furnace. To assure more accurate yields, the standard was run immediately before each coal sample. The standard values were then averaged each day, providing a daily calibration factor.

Samples. All samples were received run-of-mine condition, sealed in plastic bags. The whole allotment (5 to 10 grams) was ground with mortar and pestle in a nitrogen purge glove bag to inhibit oxidation. Homogeneity problems were encountered with some samples and these were reground.

Eighteen samples were received from various parts of the San Juan Basin - Fruitland formation, 12; Menefee formation, 4; Hog mountain tongue, 2. Table 1 shows the formation, the sample identification symbols, the well and depth (feet), and the vitrinite reflectance values (mean random reflectance values). The samples range from essentially subbituminous rank to medium-volatile bituminous. The depths of the Fruitland samples vary considerably and are not directly correlated with rank because of non-uniform heating due to an intrusion in the formation and the different well locations through out the field. For Henry AGC Fed #1, the shallower samples are from the Fruitland formation, and the deeper samples are from the Menefee formation (the well probably passes through the Pictured Cliffs and Cliff House sandstone formations). For Champ #5, the shallower sample is from the Fruitland formation, probably more north than the Henry AGC Fed #1 well, the intermediate samples are from the Hog Mountain tongue, and the deepest samples are from the Menefee formation. The maturity of the Menefee formation samples from these two wells is only slightly higher than that of the shallower Fruitland samples.

Extraction. 0.2 to 0.5 g of the coal sample were extracted in a micro-soxhlet extractor for 36 hours using either the 92% CH_2Cl_2/8% MeOH azeotrope or 100% tetrahydrofuran (THF) as the extraction media. After the extraction was complete, the extracted coal was dried *in vacuo* and the solvent with the extracted bitumen was removed under a stream of N_2 gas. Mass balances exhibited over 98% recovery for the CH_2Cl_2/MeOH extractions. The THF extraction exhibited over 100% recovery after extensive drying, indicating some permanent incorporation of the solvent into the sample.

Elemental Analyses. Table 2 lists the C, H, N, CO_2, and TOC (total organic carbon) analyses (there was not enough CH5D sample to analyze). Most of the coals have TOC levels which fall in the range of 30 to above 60 wt%, with KB5B being the richest. Two are less than 30 wt% and one, CU2A, is extremely lean in organic matter. This coal exhibits anomalous evolution behavior (see below). The coals are also very low in carbonate content (%CO_2).

T_{max} and Yield Data

Relationship between T_{max} and vitrinite reflectance. Figure 1 shows the T_{max} values at the nominal heating rate of 25°C/min measured directly on the coal samples from the San Juan Basin as a function of maturity (measured by vitrinite reflectance). Included are not only the Fruitland seam coals, but also coals from the other seams.

Except for the two coals with the lowest R_m values, all the T_{max} values fall nicely on a slightly curved line which has a positive slope with increasing R_m values. This behavior includes coals from the Fruitland, Menefee, and Hog Mountain seams. Generally two runs were performed on each coal and both runs were in good agreement, except for CU2A. The T_{max} of this coal was particularly susceptible to sample size.[5] Ten runs were made to obtain reasonably reproducible data. This coal has a very low TOC (see Table 2), and mineral matter, sample inhomogeneity, as well as a high percentage of the TOC being bitumen, could be causes for variations in the pyrolysis behavior.[6]

The coals with the lowest R_m, CH5A and HAFA, have T_{max} values which do not fall in line with the rest of the T_{max} values. Measurements on these coals and GR3A and KB5A were repeated to check reproducibility, and the results were found to be comparable to the original data. (The latter data was taken on the Pyromat II after the furnace was replaced) No reason for the outlying behavior of CH5A and HAFA is obvious from the little data we have on other properties of the coals. However, both these coals are found at the shallowest depth (300 ft above the others). In addition, the CH5A sample was from above the Hog Mountain tongue, and both

HAFA and CH5A samples are from above the Menefee formation (see Table 1). It is important to note that Michael et al.[7] found a linear relationship between R_m and T_{max} for Rock Eval measurements on coals from the San Juan basin. This result would suggest CH5A and HAFA as being well behaved and that the Menefee and Hog Mountain coals (see Figure 1) do not follow the trend.

Relationship between yield and vitrinite reflectance. The yields were also measured at the nominal heating rate of 25°C/min on the coals from the San Juan Basin, and are shown in Figure 1 as the open symbols (corresponding to the closed symbols for the T_{max} values). Because the Pyromat II has no direct method of measuring yield, these values were measured by using an AP22 standard (see experimental). For most of the data shown in Figure 1, the calibration factor from the AP22 standard was an overall average (yield method 1). For selected coals, the yields were checked more carefully, particularly if the value appeared to not follow the trend in Figure 1 (yield method 2).

The yield data shown in Figure 1 exhibits scatter, particularly for the low R_m coals. However, the yields appear to decrease with increasing R_m, with a noticeable change in the curvature around R_m of 0.9%. This is even more noticeable when considering only the Fruitland formation coals. (GR3B does not really follow this trend as well as one determination for CU2A. We had significant problems with every aspect of CU2A, and have little confidence in the reproducibility. Alternatively, it may contain primarily migrated bitumen.) The trend of decreasing yield above R_m of 0.9% has been seen for the Fruitland seam previously.[6]

Effect of bitumen extraction on pyrolysis yields. Four Fruitland coals, CH5A, MOAB, KB5B, and CU5A, were extracted with organic solvents to remove native bitumen and the pyrolysis yields were determined. Table 3 shows a summary of these data and compares them with the data on the corresponding unextracted coal. In all cases, the extraction reduces the pyrolysis yield. The magnitude depends upon the coal and the extraction solvent. The extracted pyrolysis yields as percentage of unextracted pyrolysis yield are: CH5A, 79; CH5A (THF extraction), 82; MOAB, 92; KB5B, 95; CU5A, 65. The extraction appears to have less effect with increasing R_m except for CU5A, which has the highest R_m of the samples studied. This behavior is opposite to the pyrolysate yields themselves which exhibit a decrease around R_m of 0.9%.

Because we had no previous experience with these coals, we selected 92% CH_2Cl_2/8% MeOH as the extraction solvent because of its effectiveness in extracting shales, the reduced likelihood of coal structure damage due to swelling, and minimal irreversible binding. The extraction yields using this solvent calculated from the weight of extracted bitumen were: CH5A, 4.4%; MOAB, 4.1%; KB5B, 4.8%; CU5A, 4.2%. However, these yields seem relatively low compared to bitumen yields for other coals, so THF was selected as an alternate. This solvent has a higher solubility parameter, and could possibly extract more native bitumen. The yield for CH5A using 100% THF as the extraction solvent was 6.9%, which is not a significantly higher to cause re-extraction of the samples. Solvents such as pyridine were ruled out because of their destructive interactions with the coal structure and the noted irreversible binding.[7]

Qualitatively, the native-bitumen extraction yields are consistent with the amount the pyrolysis yields are reduced upon extraction for all the coals except CU5A. For this coal, the pyrolysis yield is reduced substantially more than would be expected from the extraction yield. The reasons for this are not clear. CU5A is the most mature sample of the group and has one of the lowest pyrolysis yield based on bitumen recovery. In addition, all the extractions of CU5A (four) showed a mass balance of over 100%, unlike the other samples, indicating solvent was incorporated into the coal structure, and suggesting the coal network was being much more affected by the extractions than the other coals.

Kinetics of Evolution of Organic Materials by Pyrolysis

Fruitland Coals. Four Fruitland coals, CH5A, MOAB, KB5B, CU5A, were examined to determine their kinetic parameters for hydrocarbon evolution. These coals were picked because their range in R_m covers from the least to most mature of the samples (see Table 1). Figure 2 shows the kinetic parameters for the discrete and approximate analyses from the best kinetic sets for each coal. The best kinetic set was chosen from multiple runs and multiple determinations, primarily from the agreement of the approximate and the discrete parameters, as well as the least squares analysis of the fits.

The best kinetic sets show some interesting trends. The parameters for the lower rank coals are all very similar. CH5A has E_{approx} and principal $E_{discrete}$ slightly higher than MOAB and KB5B. CU5A stands out as having the highest R_m of the samples studied and distinctly different kinetic parameters (higher E_{approx} and principal $E_{discrete}$). This appears to follow the behavior seen before in the kinetic studies of Argonne premium coals,[8] which show a decrease in activation energy with increasing rank for the lower rank coals, and an increase in activation energy with increasing rank for the higher rank coals.

Figure 2 also shows the fits of the evolution data using the discrete distribution model. The fits for CH5A, MOAB, and KB5B look very good. However, the fits for CU5A look significantly poorer. This will be discussed below.

Extracted Fruitland Coals. To understand the effects of native bitumen on the kinetics parameters of these coals, CH5A, KB5B, MOAB, and CU5A were extracted with organic solvents and the pyrolysis kinetics were determined from multiple-heating rate experiments. The best kinetic sets are listed in Table 4.

As in the case for the unextracted coals, the lower rank coals all have very similar kinetic parameters. E_{approx} and principal $E_{discrete}$ are slightly higher for CH5X. As the rank increases, E_{approx} and principal $E_{discrete}$ are slightly lower for both MOAX and KB5X, and then is significantly higher for CU5X. This behavior is almost identical to the behavior of the unextracted coals.

Comparing the parameters in Figure 2 and Table 4 shows the kinetics for the unextracted and corresponding extracted coals are within experimental error. CH5X and CH5A show the most difference. Noting the possibility of compensating A values for the lower activation energy values for CH5X, the discrete kinetic parameters were recalculated for CH5X holding the A value fixed at 1.74×10^{15}. Table 5 shows these results. Although the least squares fits were not as good as for the CH5X kinetic set, the resulting discrete parameters were almost identical to those of the unextracted CH5A coal.

The similarity of the parameters for the unextracted coals and the corresponding extracted coals indicates the extraction does little to effect the kinetic parameters. The biggest differences are seen in the calculated T_{max} values at the heating rate of 25°C/min. The extracted coals yield values which are slightly higher for the lower ranks, and essentially identical for the higher rank coals. However, this difference is probably not significant enough to confidently say the extraction affects laboratory pyrolysis evolution kinetics, or that extraction is necessary in these cases to obtain valid kinetics.

This was not the case for CU5A, where the kinetic determinations were not as easy to interpret. The choice for the best kinetic set required several determinations, as well as considering the extracted data also. Figure 3 shows a comparison of extracted and unextracted CU5A at the nominal heating rate of 25°C/min. Obvious is the removal of the low temperature evolving material in the extracted sample. This had a significant effect on discrete kinetic parameters. Also, the σ values in Figure 2 and Table 4 show this extraction affects the peak width of evolving materials in the kerogen pyrolysis range.

As stated in the yield section, CH5A was also extracted with THF. The best kinetic set is shown in Table 5, which shows that the THF extraction had little effect on the kinetic parameters, where the values are within experimental error of the CH_2Cl_2/MeOH extraction parameters.

Conclusions

For the San Juan Basin coals in this study:

1) T_{max} increases systematically with increasing maturity (as measured by vitrinite reflectance).

2) Total pyrolysate yield increases with increasing maturity until a R_m of approximately 0.9%. After this, the yield begins to decrease rapidly.

For the Fruitland seam coals in this study:

1) Extraction with 92% CH_2Cl_2/8% MeOH removes approximately 4% by weight of total sample. This qualitatively agrees with the reduction of pyrolysis yield upon extraction, except for CU5A.

2) Extraction of CH5A with 100% THF showed modest increase in bitumen yield over the 92% CH_2Cl_2/8% MeOH extraction, but showed no decrease in pyrolysis yield. This suggests THF is being incorporated into the coal.

3) Kinetic calculations of CH5A, MOAB, and KB5B, showed similar kinetic parameters. CU5A, however, had much higher activation energies.

4) Kinetic calculations of the extracted CH5A, MOAB, and KB5B showed similar kinetic parameters. Extracted CU5A, however, had much higher activation energies.

5) Kinetic parameters of the extracted CH5A, MOAB, and KB5B coals were almost identical to the parameters of the corresponding unextracted coal indicating extraction does little to effect the coal structure and is probably not necessary for these determinations.

6) Kinetic calculations for CU5A showed large differences between approximate and discrete parameters. The kinetic parameters of the extracted data set were used to resolve these discrepancies which suggests extraction is necessary for this coal.

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Table 1. Selected information on coals from the San Juan Basin.

Sample ID	Formation	Depth (feet)	Vitrinite Reflectance (%R_m)
HAFA[a]	Fruitland	1528-1534	0.46
HAFB[a]	Menefee	3049-3054	0.57
HAFC[a]	Menefee	3800-3810	0.58
CH5A[b]	Fruitland	950-960	0.44
CH5B[b]	Hog Mountain	1880-1890	0.52
CH5C[b]	Hog Mountain	1910-1920	0.49
CH5D[b]	Menefee	3170-3180	0.54
CH5E[b]	Menefee	3210-3220	0.54
MOAA[c]	Fruitland	2927-2937	0.76
MOAB[c]	Fruitland	3085-3106	0.82
KB5A[d]	Fruitland	3046-3056	0.82
KB5B[d]	Fruitland	3169-3184	0.93
GR3A[e]	Fruitland	2520-2540	0.62
GR3B[e]	Fruitland	2540-2550	0.66
CU2A[f]	Fruitland	3960-3990	1.08
SJ8A[g]	Fruitland	3150-3160	1.22
SJ8B[g]	Fruitland	3148-3158	1.24
CU5A[h]	Fruitland	4180-4200	1.30

Wells:
a. Henry AGC Fed #1 (Yates Petroleum Co.). b. Champ #5 (Dugan Petroleum Co.). c. Moore A #8 (Amoco Production Co.). d. Kernaghan B #5 (Amoco Production Co.). e. Grenier #103 (Meridian Oil). f. Carracas Unit 23A #2 (Nassau Resources). g. San Juan 32-5 #108 (Meridian Oil). h. Carracas Unit 17B #15 (Nassau Resources).

Table 2. Selected elemental analyses for coals from the San Juan Basin.

Sample	%C	%H	%N	$\%CO_2$	TOC
HAFA	41.81 (0.35)	3.78 (0.14)	1.26 (0.10)	0.96	41.55
HAFB	40.22 (0.09)	3.63 (0.03)	1.26 (0.22)	0.53	40.08
HAFC	59.74 (1.33)	4.69 (0.06)	1.43 (0.22)	0.47	59.61
CH5A	51.88 (0.20)	3.99 (0.06)	1.12 (0.09)	2.65	51.15
CH5B	61.86 (0.06)	4.83 (0.19)	1.49 (0.24)	0.62	61.69
CH5C	46.08 (1.19)	3.73 (0.12)	1.08 (0.01)	0.72	45.88
CH5D	na	na	na	na	na
CH5E	26.11 (31.7)	2.30 (0.10)	2.19 (0.09)	0.63	25.94
MOAA	38.27 (3.83)	3.10 (0.06)	1.10 (0.16)	2.31	37.64
MOAB	63.21 (1.93)	4.12 (0.07)	1.53 (0.04)	0.88	62.97
KB5A	60.23 (1.67)	4.41 (0.26)	1.43 (0.19)	1.41	59.85
KB5B	64.09 (1.08)	4.48 (0.14)	1.89 (0.27)	1.35	63.72
GR3A	18.41 (0.34)	1.95 (0.01)	0.63 (0.04)	1.76	17.93
GR3B	55.69 (2.28)	4.96 (0.89)	1.62 (0.06)	1.65	55.24
CU2A	1.93 (0.06)	0.52 (0.08)	nd	2.91	1.14
SJ8A	36.35 (0.56)	2.65 (0.13)	1.17 (0.09)	0.95	36.09
SJ8B	33.42 (1.29)	2.37 (0.06)	0.88 (0.03)	1.33	33.06
CU5A	56.29 (0.58)	3.26 (0.06)	1.19 (0.07)	0.12	55.75

na. Not enough sample to analyze. nd. Analyzer problem with N determination

Table 3. Summary of yield data by Pyromat II micropyrolysis for selected coals and bitumen-extracted coals from the San Juan Basin at the nominal heating rate of 25°C/min.

Coal	Extraction Solvent	Yield, mg pyrolysate/ g coal	Yield, mg pyrolysate/ g TOC
CH5A	none	131	255
CH5A	92% CH_2Cl_2/8% MeOH	104	na
CH5A	100% THF	108	na
MOAB	none	191	303
MOAB	92% CH_2Cl_2/8% MeOH	175	na
KB5B	none	192	303
KB5B	92% CH_2Cl_2/8% MeOH	182	na
CU5A	none	91	163
CU5A	92% CH_2Cl_2/8% MeOH	59	na

na = not enough sample to measure TOC

Table 4. Approximate and discrete kinetic parameters from the best kinetic sets selected for extracted CH5A (CH5X), MOAB (MOAX), KB5B (KB5X), and CU5A (CU5X) coals.

Sample	CH5X	MOAX	KB5X	CU5X
Approximate E,[a] kcal/mol	55.9 (0.05)	55.2 (0.09)	55.2 (0.09)	63.2 (0.20)
Approximate A, 1/sec	4.83×10^{14}	9.7×10^{13}	8.64×10^{13}	5.52×10^{15}
Approximate σ, % of E	3.14	2.34	2.40	3.16
Discrete E, % of Total				
41 kcal/mol			0.09	
42 kcal/mol	0.49			
43 kcal/mol	0.33		0.25	
44 kcal/mol	0.66	0.11	0.67	
45 kcal/mol		0.01	0.63	
46 kcal/mol	0.24	0.44	1.00	
47 kcal/mol	0.29	0.19	1.07	0.80
48 kcal/mol	0.42	1.41	1.31	
49 kcal/mol	0.05	0.23	1.44	0.56
50 kcal/mol	1.03	1.86	1.84	0.74
51 kcal/mol	0.38	0.40	1.02	0.80
52 kcal/mol	1.74	0.89	1.71	0.78
53 kcal/mol	3.65	3.42	1.13	0.68
54 kcal/mol	5.26	0.35	8.15	1.78
55 kcal/mol	16.70	26.26	25.63	0.39
56 kcal/mol	21.12	22.30	20.77	2.72
57 kcal/mol	16.08	17.21	12.04	0.18
58 kcal/mol	11.98	5.17	4.56	1.67
59 kcal/mol	4.91	5.79	6.54	0.89
60 kcal/mol	3.41	3.17		10.45
61 kcal/mol	3.17	1.77	4.83	15.21
62 kcal/mol	2.03	2.10	0.10	16.02
63 kcal/mol	1.36	0.43		11.71
64 kcal/mol	2.55	3.02	4.74	8.99
65 kcal/mol				5.99
66 kcal/mol	0.89			3.03
67 kcal/mol	1.73	3.47		2.86
68 kcal/mol				6.11
69 kcal/mol				
70 kcal/mol				
71 kcal/mol				7.65
Discrete A, 1/sec	6.47×10^{14}	1.65×10^{14}	1.13×10^{14}	2.40×10^{15}
T_{max}, °C, at 25°C/min	468.06	491.78	494.94	514.51

a ± error in kcal/mol in parentheses

Table 5. Approximate and discrete kinetic parameters from the best kinetic sets selected for CH5A, CH5X (92% CH_2Cl_2/8% MeOH extracted CH5A), CH5X with fixed A (from CH5A determination), and CH5T (THF extracted CH5A).

Sample	CH5A	CH5X	CH5X fixed A	CH5T THF extracted
Approximate E,[a] kcal/mol	56.7 (0.07)	55.9 (0.05)	55.9 (0.05)	55.7 (0.03)
Approximate A, 1/sec	9.99×10^{14}	4.83×10^{14}	4.83×10^{14}	4.06×10^{14}
Approximate σ, % of E	3.58	3.14	3.14	3.05
Discrete E, % of Total				
42 kcal/mol		0.49		1.14
43 kcal/mol		0.33		0.85
44 kcal/mol		0.44	0.28	0.18
45 kcal/mol			0.66	1.95
46 kcal/mol		0.46		0.68
47 kcal/mol		0.29	0.24	
48 kcal/mol		0.42	0.23	0.99
49 kcal/mol		0.05	0.39	
50 kcal/mol	2.41	1.03	0.15	1.65
51 kcal/mol	1.42	0.38	0.68	0.13
52 kcal/mol	2.76	1.74	0.79	3.32
53 kcal/mol	1.53	3.65	1.02	3.34
54 kcal/mol	5.92	5.26	3.48	10.56
55 kcal/mol	5.87	16.70	4.28	**23.76**
56 kcal/mol	12.80	**21.12**	11.59	15.41
57 kcal/mol	**19.60**	16.08	**20.41**	16.20
58 kcal/mol	14.07	11.98	17.40	4.57
59 kcal/mol	16.02	4.91	13.97	4.90
60 kcal/mol		3.41	7.40	3.51
61 kcal/mol	7.72	3.17	3.97	0.98
62 kcal/mol	0.40	2.03	2.79	2.62
63 kcal/mol	3.52	1.36	3.49	0.87
64 kcal/mol	0.04	2.55		
65 kcal/mol	2.39		3.88	2.38
66 kcal/mol		0.89	0.03	4.71
67 kcal/mol	1.85	1.73		0.82
68 kcal/mol	0.21		2.84	7.97
69 kcal/mol				
70 kcal/mol	1.48			
71 kcal/mol				7.27
Discrete A, 1/sec	1.74×10^{15}	6.47×10^{14}	1.75×10^{15}	4.06×10^{14}
T_{max}, °C, at 25°C/min	464.48	468.06	468.06	468.87

a ± error in kcal/mol in parentheses

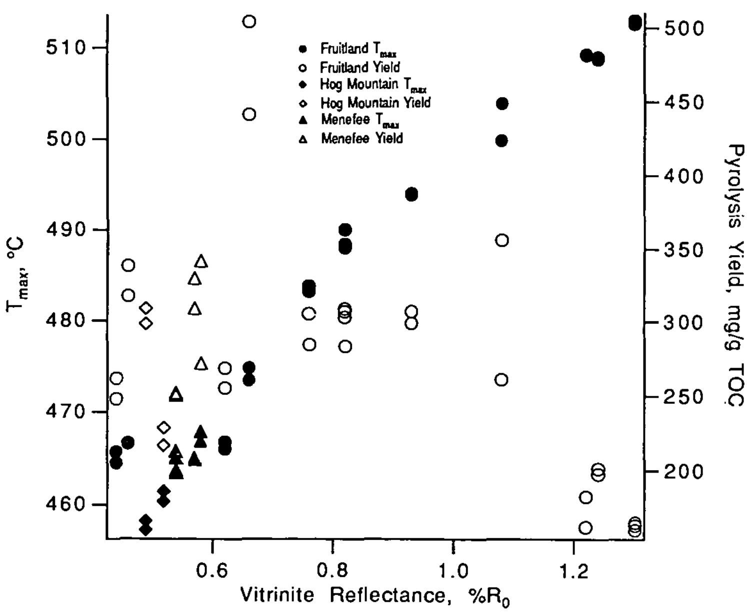

Figure 1. Relationship of maximum rate of evolution (T_{max}) and pyrolysate yield (mg/g TOC) with vitrinite reflectance ($\%R_m$) at the nominal heating rate of 25°C/min for selected coals from the San Juan Basin.

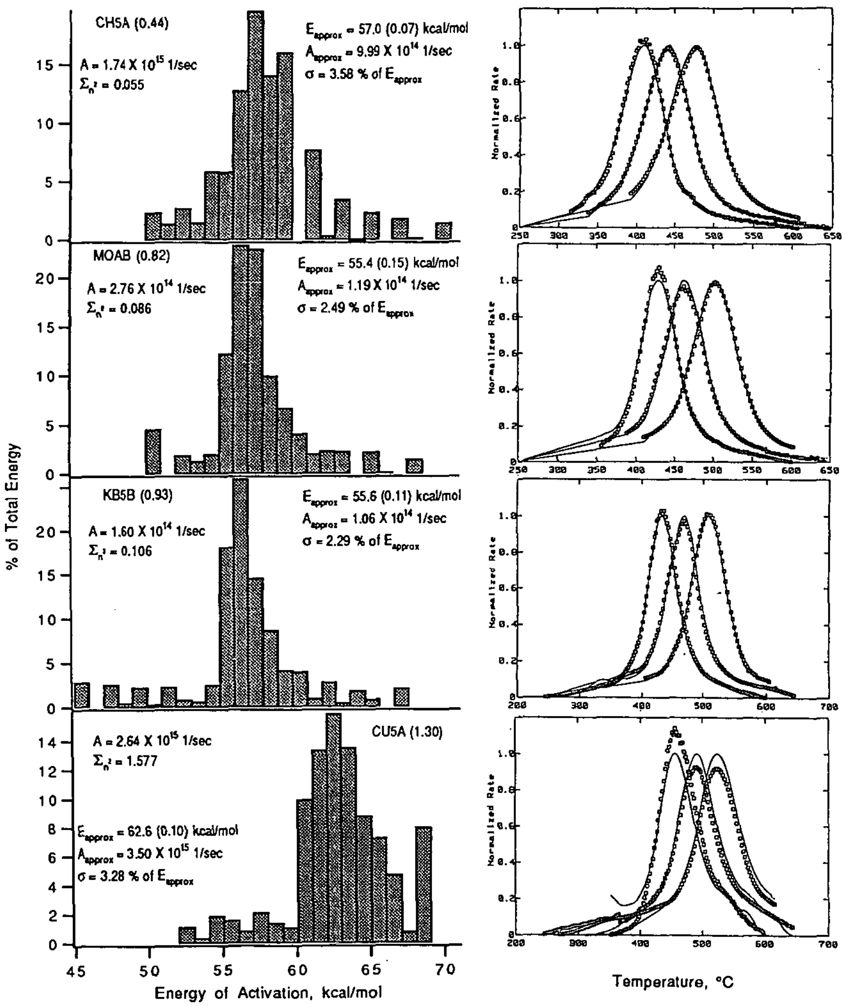

Figure 2. Approximate and discrete kinetic parameters for CH5A, MOAB, KB5B, and CU5A coals (left side) and corresponding evolution data fits from the discrete kinetic analysis (right side).

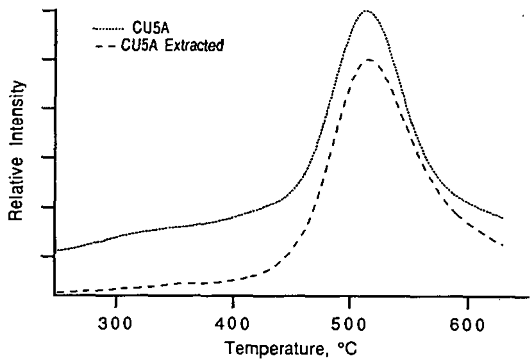

Figure 3. Evolution profiles for CU5A and extracted CU5A coals at the nominal heating rate of 25°C/min.